Faculty of Manufacturing Engineering

THE EFFECTS OF ALUMINA ON THE DENSE CALCIUM PHOSPHATE SYNTHESIZED FROM EGGSHELL WASTE

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DECLARATION

I declare that this thesis entitled "The Effects of Alumina on The Dense Calcium Phosphate Synthesized from Eggshell Waste" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : …….....

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APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master in Manufacturing Engineering (Materials).

Signature	:	…….....
Supervisor's Name	:	……..……..
Date	:	……..……..

DEDICATION

Dedicated to all my beloved Muslim brothers and sisters throughout the world struggling to gain Allah S.W.T's pleasures (Redha) in this Life and for the Hereafter

ABSTRACT

Eggshell (ES) wastes were processed and used as starting materials for the synthesis of calcium phosphates (CaP) such as hydroxyapatite (HA) and tricalcium phosphates (TCP). Hydrothermal and mechanochemical synthesis methods were applied to synthesize hydroxyapatite and hydroxyapatite-alumina bioceramic composite powders with ultrafine microstructures from both eggshell wastes and chemical calcium precursors to develop bioceramics with enhanced mechanical properties for medical applications. Despite its attractive, bioactive and biocompatibile properties, CaP has been limited in applications due to the poor processability and mechanical strengths of the material. To further toughen the CaP matrix, nanocrystalline alumina (Al_2O_3) with the addition amounts of 15wt.% and 35wt.% was introduced. CaP in the form of dense compacts was prepared by uniaxial pressing and sintered through pressureless sintering method in air atmosphere at various sintering temperatures. The effects of the type of calcium sources, the synthesis pH conditions, the Al_2O_3 incorporation and the sintering temperature on the phase behaviour and the mechanical properties of the developed ceramic bodies were evaluated. The presence of HA and Al_2O_3 phase in the powder synthesis was confirmed through XRD, FT-IR and TGA analyses. However, the major phase detected in the developed dense compacts after sintering conducts was TCP. FESEM and EDX assessments showed nano-sized rods and spherical morphologies with corresponding element analysis of the synthesized powders. SEM analyses were used to observe the morphology and densification behaviour of the bioceramic compacts. Density, porosity, compression, elasticity, microhardness and fracture toughness tests were used to monitor the physical and mechanical properties. Statistical analysis using MINITAB was used to summarize the mechanical evaluations. The leading mechanical attributes were achieved by dense bioceramics synthesized from ES-based calcium precursor at pH 9 conditions after being sintered at 1250°C. Al_2O_3 reinforcements were preferred in small quantities to achieve better mechanical properties. The highest measurement of Vickers hardness and facture toughness was acquired through the sample that was synthesized at alkaline conditions, 15wt% alumina content and after being sintered at 1250°C with values of 4.76 GPa and 4.12 $MPam^{1/2}$ respectively. Sintering temperature was concluded to be the most influencing variable parameter for every evaluation particularly for the enhancement of mechanical strength of the developed bioceramics.

ABSTRAK

Sisa kulit telur telah diproses dan digunakan sebagai bahan pemula untuk sintesis fosfat kalsium (CaP) seperti hydroxyapatite (HA) dan fosfat trikalsium (TCP). Kaedah sintesis secara hidroterma dan mekano-kimia telah digunakan untuk mensintesis hidroksiapatit dan serbuk komposit bioseramik hidroksiapatit-alumina dengan mikrostruktur ultrahalus daripada kedua-dua sisa kulit telur dan pelopor kalsium berkimia untuk membangunkan bioseramik dengan peningkatan sifat mekanik untuk aplikasi perubatan. Meskipun bersifat penarik, bioaktif dan serasi secara biologi, penggunaan CaP adalah terhad kerana kekurangan dari segi kebolehan daya pemprosessan dan kekuatan mekanikal bahan tersebut. Bagi menguatkan matriks CaP, alumina (Al_2O_3) yang bersifat nanokristalin dengan pertambahan 15wt.% dan 35wt.% dicampurkan. CaP dalam komponen yang padat telah disediakan melalui kaedah tekanan ekapaksi dan disinter melaui kaedah pensinteran tanpa tekanan pada atmosfera udara yang pelbagai suhu pembakarannya. Kesan jenis sumber kalsium, keadaan pH semasa sintesis, penampahan kandungan Al_2O_3 dan suhu pensinteran terhadap pola fasa dan sifat-sifat mekanik bioseramik yang disediakan dinilai. Kehadiran fasa-fas HA dan Al_2O_3 dalam serbuk sinstesis telah dikenal pasti melalui analisa XRD, FT-IR dan TGA. Namun begitu, fasa perubahan utama yang dikesan dalam komponen padat selepas pensinderan dijalankan ialah TCP. Penilaian terhadap FESEM dan EDX menunjukkan morfologi rod bersaiz nano yang berbentuk sfera konsisten dengan analisa unsur sepadan pada serbuk yang telah disintesiskan. Analisis terhadap SEM digunakan untuk memperhatikan pola morfologi dan ketumpatan komponen bioseramik. Ujian ketumpatan, keliangan, pemampatan, keanjalan, kekerasan mikro dan keliatan patah digunakan untuk memantau ciri-ciri fizikal dan mekanikal. Analisis statistik menggunakan MINITAB juga digunakan untuk merumuskan penilaian mekanikal. Ciri-ciri utama mekanikal dicapai oleh bioseramik padat yang telah disintesis daripada sisa kulit telur sebagai pelopor kalsium pada kondisi pH 9 dan selepas disinter pada suhu 1250 °C. Bagi mencapai ciri-ciri mekanikal yang lebih baik hanya kuantiti Al_2O_3 yang kecil diperlukan. Bacaan tertinggi bagi kekerasan Vickers dan keliangan padat telah diperolehi oleh sampel ES-9-15A-1250 yang disintesis dengan kondisi alkali, 15wt% kandungan alumina dan setelah disinter pada suhu 1250 °C adalah masing-masing bernilai 4.76 GPa dan 4.12 $MPam^{1/2}$. Suhu pensinteran dikonklusikan sebagai parameter pemboleh ubah paling berpengaruh untuk setiap penilaian terutamanya bagi peningkatan kekuatan mekanikal bioseramik yang telah disediakan.

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LIST OF ABBREVIATIONS

BCP	-	Bi-phasic calcium phosphate
CaP	-	Calcium phosphate
CH	-	Commercial chemical
ES	-	Eggshells
CDHA	-	Calcium-deficient hydroxyapatite
FA	-	Fluorapatite
HA	-	Hydroxyapatite
TCP	-	Tri-calcium phosphate
$(NH_4)_2HPO_4$	-	Di-ammonium hydrogen phosphate
Al_2O_3	-	Alumina
$Ca(NO_3)_2$	-	Calcium nitrate
$Ca(OH)_2$	-	Calcium hydroxide
$CaCO_3$	-	Calcium carbonate
CaO	-	Calcium oxide
$CaTiO_3$	-	Calcium titanate
CH_3COOH	-	Acetic acid
CO_2	-	Carbon dioxide
CO_3	-	Carbonate
HPO_4	-	Hydrogen phosphate
MgO	-	Magnesium oxide
$NH_4H_2PO_4$	-	Ammonium di-hydrogen phosphate
NH_4OH	-	Ammonium solution
P_2O_7	-	Pyrophosphate
SO_4	-	Sulphate
TiO_2	-	Titanium dioxide
ZrO_2	-	Zirconia
Ca^{2+}	-	Calcium ion
OH^-	-	Hydroxide ion

PO_4^{3-}	-	Phosphate ion
C	-	Carbon
Cl	-	Chlorine
Cu	-	Copper
F	-	Fluorine
Fe	-	Iron
Mg	-	Magnesium
O	-	Oxygen
Pb	-	Lead
Si	-	Silicon
Sr	-	Strontium
dH_2O	-	Distilled water
Ca/P	-	Calcium to phosphate ion molar ratio
RIR	-	Relative intensity ratio
FWHM	-	Full width at half maximum
T_C	-	Crystallization temperature
T_G	-	Glass transition temperature
T_M	-	Melting temperature
X_C	-	Degree of crystallization
X_S	-	Crystallite size
E	-	Elasticity
FS	-	Flexural strength
HV	-	Vickers's hardness
K_{IC}	-	Fracture toughness indentation
TS	-	Tensile Strength
ATR	-	Attenuated Total Refractance
DSC	-	Differential Scanning Calorimetry
EDX	-	Energy Dispersive X-Ray
FESEM	-	Field Emission Scanning Electron Microscopy
FT-IR	-	Fourier Transformed Infrared
SEM	-	Scanning Electron Microscopy
TG/DTA	-	Thermo-gravinomety and Differential Thermal Analyser
XRD	-	X-Ray Diffraction
MINITAB	-	Minitab Statistical Software
JCPDS	-	Joint Committee on Powder Diffraction Standards

3D	-	Three dimensions
NA	-	Not available
Ref.		Reference

LIST OF SYMBOLS

%	-	Percentage
a		Rupture Strength
Å	-	Angstrom
Dia.	-	Diameter
h	-	Hour
K	-	Scherer's constant = 0.94
min	-	Minute
L		Length
n	-	Order of reflection
º	-	Degree
ºC/min	-	Degree Celsius per minute
pH	-	Measurement of the acidity or basicity
rpm	-	Revolution per minute
kgf	-	Kilogram force
T	-	Temperature
V	-	Valley between peaks
wt. %	-	Weight percentage
X	-	Times magnification
α	-	Alpha crystal polymorph
β	-	Beta crystal polymorph
θ	-	Angle of diffraction
λ	-	Wavelength

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AWARDS

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